

AD-765 423

EXPERIMENTAL NYLON 6 FOR PERSONNEL ARMOR

Richard E. Mayer

Allied Chemical Corporation

Prepared for:

Army Natick Laboratories

December 1972

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

AD 765423

AD

TECHNICAL REPORT

73-28-CE

EXPERIMENTAL NYLON 6 FOR PERSONNEL ARMOR

by

Richard E. Mayer

Allied Chemical Corporation

Petersburg, Virginia

Contract No. DAAG-17-70-C-0029

Approved for public release ;
distribution unlimited.

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield VA 22151

December 1972

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760



Clothing & Personal Life Support Equipment
Laboratory

TS-184

Approved for public release;
distribution unlimited.

AD _____

TECHNICAL REPORT
73-28-CE

EXPERIMENTAL NYLON 6 FOR PERSONNEL ARMOR

By

Richard E. Mayer

Allied Chemical Corporation
Petersburg, Virginia

Contract No. DAAG17-70-C-0029

Project Reference:
1TO62105A329

Series: C&PLSEL-184

December 1972

Clothing and Personal Life Support Equipment Laboratory
U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts 01760

125

FOREWORD

Polyamide type yarns have proved to be the best candidates for high impact resistance in fabric or felt form. This is especially true in matters of ballistic resistance. However, for many years Nylon 6 or Caprolactam nylon, did not provide equal ballistic resistance to Nylon 6,6. This difference in performance was generally attributed to variations in melting points of the two types of fiber. More recently, Allied Chemical Corporation achieved new characteristics in Nylon 6 which made it competitive ballistically at the same areal density with the improved forms of Nylon 6,6 as produced by several different manufacturers. Accordingly, the program reported was sponsored by the US Army Natick Laboratories under Contract No. DAAG17-70-C-0029 with Allied Chemical Corporation, in an effort to determine whether the performance of the new type Nylon 6 could be further optimized by variations in molecular weight, molecular weight distribution, orientation and crystallinity. The results, although negative in respect to the goals sought, nevertheless show that an investigation of fundamentally different types of fiber is needed to obtain significant improvements in tenacity, work to rupture and attendant increases in impact resistance.

The project officers for this investigation conducted under Materials Research Project 1TO62105A329-02 were Mr. Frank J. Rizzo, Chief, Textile Research and Engineering Division, and Dr. Roy Laible, Chief, Textile Research Section, both of the US Army Natick Laboratories.

CONTENTS

	<u>Page</u>
LIST OF TABLES	iv
LIST OF FIGURES	v
ABSTRACT	vi
1. INTRODUCTION	1
2. BACKGROUND	2
3. APPROACH	8
4. EXPERIMENTAL	10
Phase I	10
a. Polymer Preparation	10
b. Yarn Preparation	12
c. Woven Fabric Preparation	12
d. Felt Preparation	15
e. Ballistic Testing	18
1. Woven Fabric	18
2. Felts	18
Phase II	18
a. Polymer Preparation	18
b. Yarn Preparation	21
c. Woven Fabric Preparation	21
d. Felt Preparation	21
e. Ballistic Testing	21

CONTENTS (cont'd)

	<u>Page</u>
5. Discussion	27
a. Woven Fabrics	27
b. Felts	28
6. Conclusions	30
7. Recommendations	31
8. References	32

LIST OF TABLES

I Test Program	9
II Properties of Nylon 6 Undrawn Yarn	11
III Properties of Nylon 6 Drawn Yarns	13
IV Properties of Nylon 6 Drawn Yarns Prepared for Ballistic Felts	14
V Physical Properties of Woven Ballistic Fabric Per MIL-C-12369E-(GL)	16
VI Percent Crystallinity of Samples	17
VII Ballistic Properties of Woven Fabrics	19
VIII Ballistic Properties of Needle-Punched Felts	20
IX Properties of Nylon 6 Undrawn Yarns Prepared for Ballistic Studies	22
X Properties of Nylon 6 Drawn Yarns Prepared for Ballistic Studies	23

DOCUMENT CONTROL DATA - R & D

AD-765423

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) US ARMY NATION LABORATORIES NATION, MASS.		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP	
3. REPORT TITLE EXPERIMENTAL NYLON 6 FOR PERSONEL ARMOR			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report			
5. AUTHOR(S) (First name, middle initial, last name) Richard E. Hayer			
6. REPORT DATE December 1962		7a. TOTAL NO. OF PAGES 3641	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO. DAAG17-70-C-0029		9a. ORIGINATOR'S REPORT NUMBER(S) TR 73-25-CE	
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
13. ABSTRACT The work, conducted under contract by Allied Chemical Corporation, was an effort to determine whether the performance of the new type Nylon 6 could be further optimized by variations in molecular weight, molecular weight distribution, orientation and crystallinity. The results, although negative in respect to the goals sought, nevertheless show that an investigation of fundamentally different types of fiber is needed to obtain significant improvements in tenacity, work-to-rupture, and attendant increases in impact resistance.			

DD FORM 1473

REPLACES DD FORM 1473, 1 JAN 62, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
TESTS	8					
BALLISTIC PROPERTIES	8,9		7			
NYLON 6 YARN	9		9			
YARNS	9		9			
FABRICS	9		9			
FABRIC LAMINATES	9		9			
FELTS	9		9			
STAPLE FIBERS	9		9			
EVALUATION	8					
BOEY LUMOR	4		4			
MOLECULAR WEIGHT			6			
WEIGHT (MASS)			6			
ORIENTATION (YARN)			6			
CRYSTAL ORIENTATION			6			

UNCLASSIFIED

Security Classification

LIST OF TABLES (cont'd)

	<u>Page</u>
XI Physical Properties of Woven Ballistic Fabric Per MIL-C-12369E-(GL)	24
XII Properties of Staple Prepared for Phase II	25
XIII Ballistic Properties of Woven Fabrics	26
XIV Physical Requirements of Cloth, Ballistic, Nylon Amendment - 2 MIL-C-12369E (GL)	29

LIST OF FIGURES

1. Melt Spinning Unit	4
2. Drawtwister Arrangement	6

EXPERIMENTAL NYLON 6 FOR PERSONNEL ARMOR

1. Introduction

The effectiveness of personnel armor made from textile structures in reducing combat casualties has been recognized for some time. Since these first ballistic fabrics were evaluated, the United States Army has supported research and development activities whose objective was to provide lighter weight personnel armor with improved projectile resistance.

For several years the Army standard fragmentation vest has been based on a twelve layer, basket-weave, 14 oz./sq. yd., type 6,6 nylon fabric as the ballistic component. Recent testing of type 6 nylon yarn in the standard construction indicated this polyamide could provide fabrics with superior ballistic resistance.

To evaluate the potential of type 6 nylon, a research study was initiated to explore the effect of certain nylon 6 polymer and yarn preparation parameters on the ballistic properties of textile structures made from them. Conditions for polymer and yarn preparation were chosen to be within a commercially practical range. The investigation was conducted in two phases.

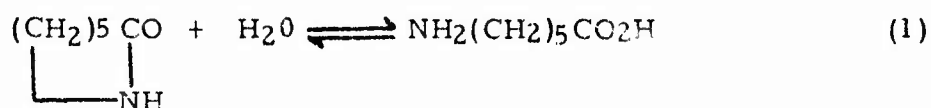
In Phase I of the study parameters were selected to determine the major effects and interactions between molecular weight, molecular weight distribution, yarn orientation and crystallinity.

Ballistic performance was studied on two types of textile structures. The first was the standard woven structure. The other was a needlepunched felt structure which has shown nearly equivalent projectile resistance in studies with the standard .22 caliber fragment simulator normally used to evaluate personnel armor.

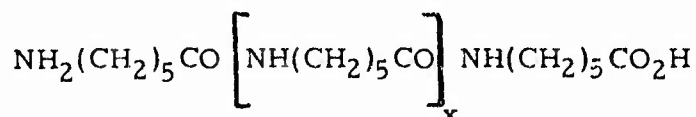
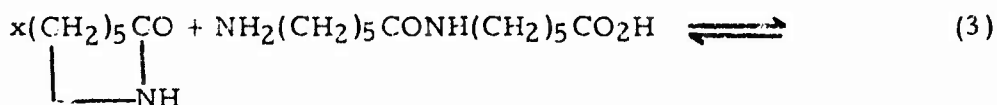
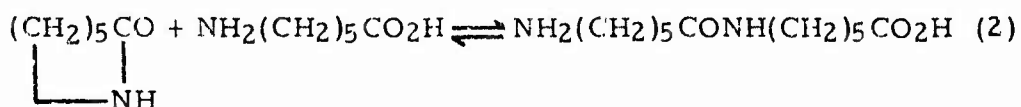
Phase II of the study was originally intended to provide additional quantities of the best fiber for fabric and felt as determined from Phase I. Since no yarn displayed superior properties, this phase was subsequently modified to be a study of the effect of filament denier.

2. Background

Polymers for type 6 nylon fibers are customarily prepared by the water initiated melt polycondensation of ϵ -caprolactam.^{1,2} The polymerization takes place in three well defined steps. First the caprolactam is hydrolyzed to ϵ -aminocaproic acid.



Hydrolysis is followed by very rapid stepwise addition of caprolactam molecules to the amino group to produce low molecular weight polymer chains as depicted below.



The final and rate determining step is the condensation of two growing chain ends with the elimination of a molecule of water.



In commercial practice the reaction is driven to completion, i. e. the formulation of high molecular weight polymer in high mass transfer reactors utilizing either inert purge gas or high vacuum for rapid removal of water. All of the reactions depicted are reversible. Thus at any given temperature and water content there exists a fixed amount

of caprolactam monomer in equilibrium with the high molecular weight chains in the polymerization melt. For condensations conducted at higher pressures this can be as high as 9 - 10% by weight of the total melt system. The presence of large amounts of monomer is not desirable for the formation of nylon 6 fibers with high tensile strength. It is often removed by leaching the solidified polymer with water prior to spinning fibers.

Nylon 6 polymer is usually converted to the high strength, twisted multifilament yarns suitable for ballistic cloth in a two step operation.¹ In the first step, spinning, the polymer is shaped into multifilament strands or filaments with low orientation and crystallinity possessing very low tensile strength. In the second step, drawing, the yarns are stretched and heated to orient and crystallize them. This latter step imparts the high tensile strength characteristic of man-made fibers.

A typical melt spinning system consists of the following items:^{1, 3, 4, 5}

- source of molten polymer
- metering pump
- filtration device
- spinneret
- quench system
- lubricator
- take-up rolls
- packaging machine or winders

Molten polymer is supplied either from a plasticating extruder, grid melter or directly from the polymerization vessel. The melt is shaped in the spinneret, a multi-orifice plate which divides the melt into individual streams called filaments. The molten filaments are quenched or solidified in a stream of air or inert gas which impinges on them directly below the spinneret. The lubricator applies a mixture of friction reducing oil, anti-static agent and water to reduce friction, lower static accumulation and provide for dimensional stability on storage. A typical nylon 6 melt spinning system is diagramed in Figure 1.

A certain amount of orientation of molecules is imparted during spinning.⁴ This orientation is usually measured by determining the birefringence of the undrawn or spun yarn. The extent of orientation

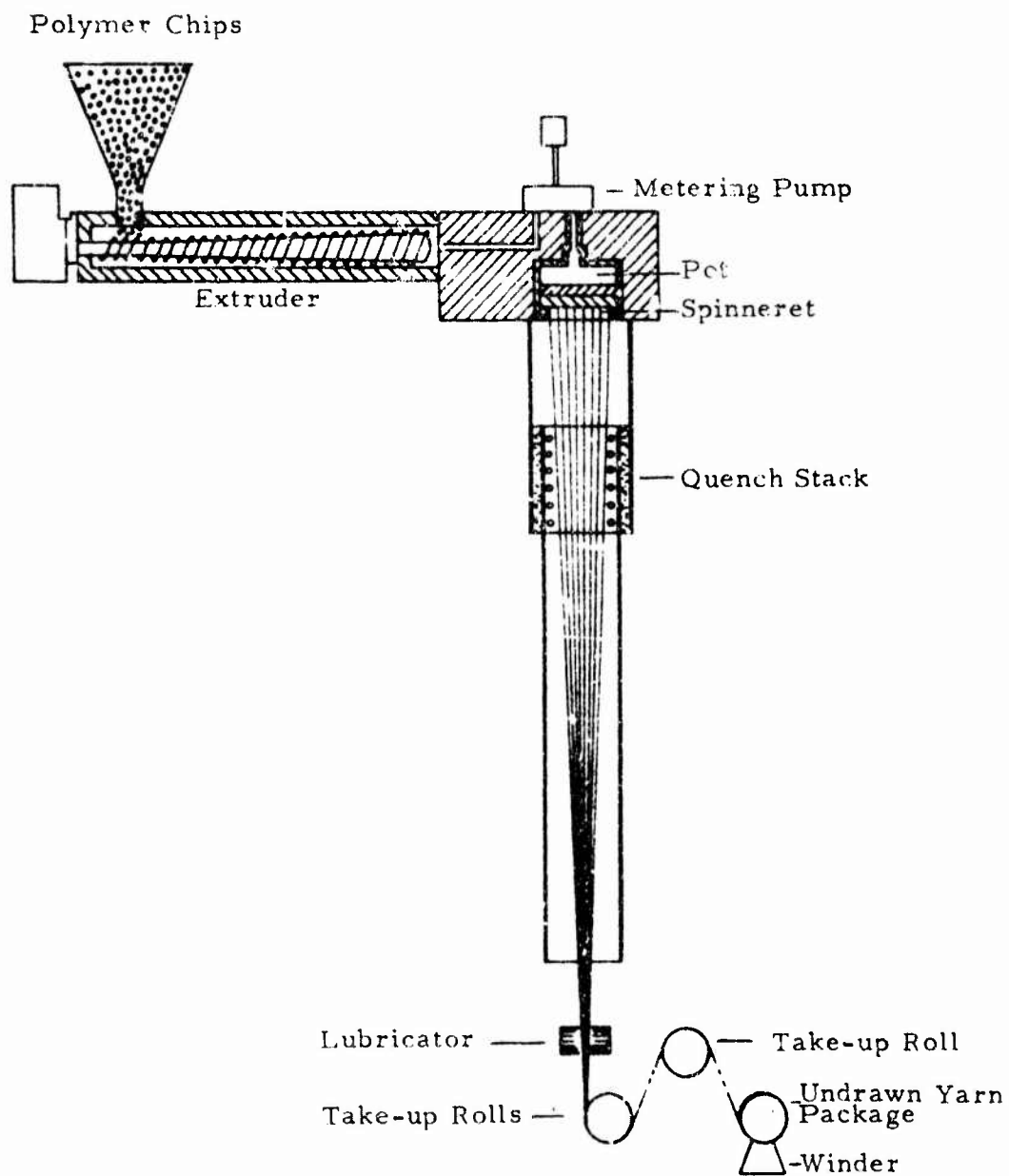


Fig. 1 - MELT SPINNING UNIT

can greatly determine the orientation and crystallinity achievable in the drawing operation and thereby the physical properties of the yarn.

Drawing apparatus vary greatly but usually consist of the following essential parts: ^{1, 3, 4, 5}

- feed rolls
- draw point localizer
- stretch heater
- take-up rolls or draw rolls
- annealing heater
- packaging apparatus

Sometimes one piece serves two purposes such as the use of a heated roll as a draw point localizer, stretch heater or annealing heater. If the drawing unit also inserts twist into the yarn, it is known as a drawtwister. A typical drawtwister for high strength nylon yarns is shown in Figure 2. The drawpoint localizer heats the yarn to a temperature at which stretching can take place uniformly. The stretch heater serves to crystallize the yarn. It is, therefore, apparent that the length and temperature of the heater can greatly determine the properties of the yarn passing over it. If additional modification of structure is desirable the yarn is often passed over an annealing heater. When annealing is done for the express purpose of reducing thermal shrinkage this device is referred to as a shrink heater. The amount of stretch or draw ratio is determined by the ration of the take-up roll speed to that of feed roll. However, there is always a certain amount of slippage on the rolls, and a better measure of draw ratio is often the ratio of the denier of the undrawn yarn to that of the drawn yarn. Orientation is even more complicated to measure, since it is the sum of the crystalline and amorphous region orientation. Since some orientation is imparted during spinning, the draw ratio does not necessarily reflect the true total orientation of the yarn.

Hayes, et.al.⁶ have discussed some factors which influence the strength of nylon yarns. Three factors appear very important: number average molecular weight, molecular weight distribution and amorphous orientation.

Numerous empirical and semi-empirical relationships between tensile strength and molecular weight of oriented polymers have been proposed. Generally it is agreed that strength depends upon number average molecular weight independent of the molecular weight distri-

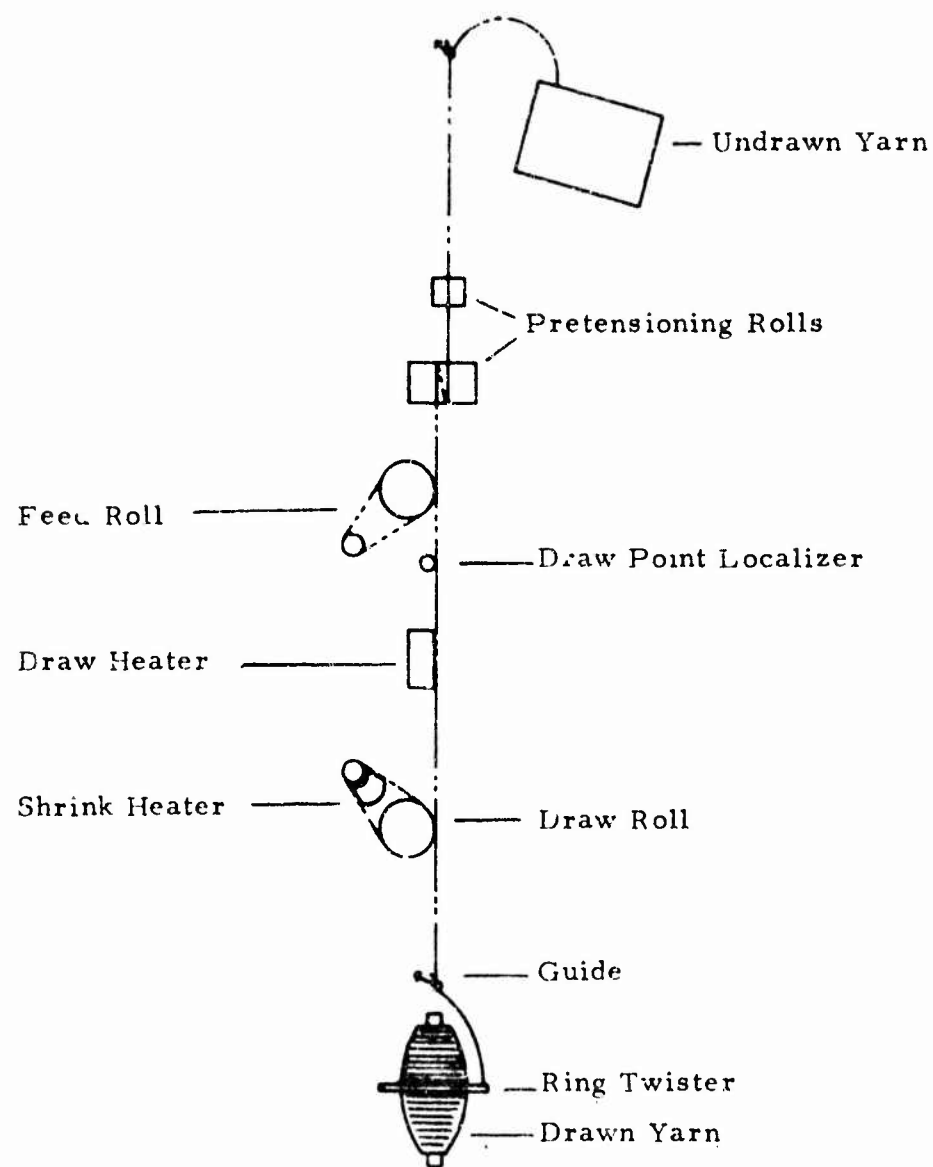


Fig. 2 - DRAWTWISTER ARRANGEMENT

bution. This relationship is commonly expressed in the form:

$$T = T_0 - a/\bar{M}_n$$

where T_0 is the strength of the polymer with infinite molecular weight and \bar{M}_n is the number average molecular weight.

Often the predicted improvement in tensile properties with increasing molecular weight is not realized because of the problems related to increased melt viscosity and slower crystallization rate. Fortunately Schaeffgen and Flory⁷ have provided insight on how to cope with this dilemma.

The hydrolytic polymerization of caprolactam is a purely random process which leads to the most probable molecular weight distribution of 2. Schaeffgen and Flory have shown that polymers prepared from A-B type monomers, of which class nylon 6 is representative, undergo a narrowing of molecular weight distribution in the presence of multifunctional terminators. They have shown that this narrowing of the molecular weight distribution is given by

$$\bar{M}_w/\bar{M}_n = \frac{1 + b(1-L)(1+Q)}{(b(1-L) + (Q+L))^2}$$

where b is the functionality of the terminator, L is the equivalents of unreacted groups per mole of A-B monomer, and Q represents the equivalents of terminator per mole of monomer. \bar{M}_w is weight average molecular weight, \bar{M}_n is number average molecular weight.

For polymers which have essentially been polymerized to completion at high molecular weight, L and Q are close to zero. This relationship may be expressed as follows:

$$\bar{M}_w/\bar{M}_n \cong 1 + 1/b$$

Melt viscosity is determined by weight average molecular weight, \bar{M}_w . It can readily be seen that higher number average molecular weights can be achieved at any \bar{M}_w with multichain terminators.

Studies at Allied Chemical Corporation have shown that fibers terminated with sebacic acid to narrow molecular weight distribution have improved tensile properties particularly at high rates of strain.

Fibers experience extremely high rates of strain in ballistic tests. It is not surprising that these fibers with narrowed distribution based on dibasic acid terminators showed good ballistic properties in initial ballistic testing. Terminators with functionality greater than 2 show only modest further improvement in tensile properties. This probably is the result of the nonlinearity of the polymer molecules produced.

3. Approach

From the discussion in the foregoing section it can readily be seen that some of the nylon 6 polymer and fiber parameters which might affect the ballistic performance of fabrics and felts are:

- number average molecular weight (\overline{M}_n)
- molecular weight distribution ($\overline{M}_w/\overline{M}_n$)
- draw ratio
- draw heater temperature
- undrawn yarn orientation
- annealing

A truly perfectly designed study of these six parameters would be extremely long and costly. For this reason it was decided that most of the yarns would be prepared from polymers of narrowed distribution terminated with sebacic acid, and drawing heater and annealing heater studies be confined to one temperature, 195°C, which usually provides the best tensile properties. The experimental plan is shown in Table I. One unterminated polymer sample was introduced to determine if the narrowed molecular weight distribution did in fact improve ballistic performance. A sample was made at lower heater temperature to establish the effect of this parameter.

The yarns were both woven into standard ballistic cloth construction and converted to standard needle punched felts. All testing was done with .22 caliber fragment simulators.

A study of the effect of filament denier on ballistic performance was made in Phase II. Deniers selected were 4, 6, 8 and 15.

Details of the experimental work are given in the section which follows.

TABLE I

TEST PROGRAM

T = Dibasic Acid Terminated

U = Untermminated

Ann. = Annealed

 \overline{M}_n = Number Average Molecular Weight

					Parameters To Be Compared to Ballistic Properties In Woven Fabrics and Felts							
Sample No.	Yarn	Staple DPF	Termination Mn x 10-3	% UE	Spun Yarn Orient.	Mol. Weight	Yarn UE	Heater Temp.	Ann. at 25 Mn	Ann. at 30 Mn	Ann. at 35 Mn	Term. vs Unt.
1	1050-175	6	T/25	18		X			X			
2	1050-175	6	T/30	18	X	X	X	X		X		X
3	1050-175	6	T/35	18		X					X	
4	1050-175	6	U/30	18								X
5	1050-175	6	T/30	14			X					
6	1050-175	6	T/30	25			X					
7	1050-175	6	T/25	Ann. 18					X			
8	1050-175	6	T/30	Ann. 18						X		
9	1050-175	6	T/35	Ann. 18							X	
10	1050-175	6	T/30	Low Biref. 18								
11	1050-175	6	T/30	Low Heater Temp. 18				X				

T = Dibasic Acid Terminated
U = Untermiated
Ann. = Annealed
Mn = Number Average Molecular Weight

4. Experimental

Phase I

a. Polymer Preparation

The technology of U.S. Patent 3,386,967⁸ was utilized to produce a dibasic acid terminated poly (ϵ -aminocaproic acid) polymer with narrowed molecular weight distribution. The batches of polymer were prepared in a 150 gallon, Dowtherm heated polymerization vessel equipped with an anchor-type agitator, nitrogen inlet and temperature recording thermocouples. The sebacic acid terminator, heat stabilizing additives and 1000 lbs. of caprolactam monomer were dissolved in a mix-tank at 70-90° and then pumped to the polymerization vessel. The polymerization vessel was purged with nitrogen to rid the atmosphere above the melt of appreciable oxygen. The charge was then heated from 90°C to 235°C in approximately 2 hours. During the heat up time approximately 20-50 psig steam was applied to the polymerization vessel to initiate the hydrolysis of caprolactam to ϵ -aminocaproic acid and initiate polymerization. At the end of the heat up cycle the steam pressure was released over a half hour period at which time the temperature was increased to 250-260°C. Viscosity was monitored by recording the agitator drive motor kilowatt response. When the proper increase in kilowatts was reached, the polymer (which contains approximately 10% extractables) was extruded through a die plate which had several round 3/16" - 5/16" diameter holes in it. The polymer ribbon was quenched in 20-50° water where it solidified. It was then cut into small cylindrical chips approximately 0.1" diameter x 0.1" long. These chips were charged to a washing and drying bin where they were washed for approximately 6-10 hours at 100°C temperatures. This washing leaches the extractables from the polymer. The extractables' content of chips after washing is approximately 1.20-1.50% by weight. Chips were then dried to equilibrium moisture and packed out in sealed cans to await spinning.

The concentration of terminator and the properties of all of the polymer batches are listed in Table II. Where a single set of properties is assigned to two batch numbers, two batches of polymers were polymerized separately and then blended, washed and dried together.

Non terminated polymers of approximately 30,000 \overline{M}_n were prepared using the same procedure except the sebacic acid was eliminated. The properties of these polymers are also listed in Table II.

TABLE II

PROPERTIES OF NYLON 6 UNDRAWN YARN

Identification	Term. - $\overline{Mn} \times 10^{-3}$ - U. E.	$\overline{Mn} \times 10^{-3}$	Carboxyl (eq/10 ⁶ g.)	Amine (eq/10 ⁶ g.)	FAV	Denier	Uster	Biref.
BAL-1, 2	T-35-18	34	44	15	106	4430	5.8	.0141
BAL-3, 4	T-30-18	30	51	16	87	4500	4.8	.0129
BAL-5, 6	T-30-25	30	51	16	90	3920	-	.0173
EAL-7, 8	T-30-14	31	51	14	88	4850	5.6	.0120
BAL-9, 10	T-30-18 Low biref.	29	53	15	88	4760	6.7	.0101
BAL-11, 12	U-30-18	30	31	36	112	4150	7.1	.0163
BAL-13, 14	T-25-18	28	58	14	72	4650	7.6	.0121
BAL-15, 16	T-30-18 Low heater temp.	30	50	16	90	4475	6.2	.0137
BAL-17, 18	T-30-18 annealed	30	52	14	90	4470	8.0	.0118
BAL-19, 20	T-25-18 annealed	27	61	14	71	4520	5.8	.0118
BAL-21, 22	T-35-18 annealed	34	42	16	119	4180	13.2	.0150

b. Yarn Preparation

The polymers were spun and drawn into the 1050 denier, 175 filament yarns with 1/2 turn of Z twist/inch shown in Tables III and IV. The odd numbered samples in the table were packaged on 3 pound pirns for subsequent conversion to staple. The even numbered samples were put on 2 pound packages for conversion to woven fabric.

A 16/1 length/diameter extruder equipped with a nylon type screw, and a Dowtherm heated spinning block was used for spinning. The block was fitted with a metering pump, pressure gauges, thermocouples and a filtration pot. The pot contained a mixture of sand as the filtration media and held a spinneret which had one hundred seventy-five capillaries .018 inches in diameter. Spinning was conducted at 280°C at a rate of 32 pounds per hour. The molten polymer was quenched by conditioned air in a concurrent flow, cylindrical quench stack of proprietary Allied Chemical Corporation design. A proprietary Allied spin finish, NXT-528, was applied to the undrawn yarn at the bottom of the quench stack as an 18% aqueous emulsion. The pick-up rate of the finish emulsion was 5% of the weight of the yarn. The yarn then passed over a set of two godet rolls and was packaged on a Leesona 959 winder.

The undrawn yarn was stored several hours to permit it to equilibrate with the moisture in the conditioned room air and then drawn at a rate of 1,000 feet per minute on a Rieter J/54 drawtwister. The yarn was drawn by passing it from a feed roll around a 1 inch diameter draw pin, then over a 6 inch stretch heater maintained at 195 ± 2°C to a draw roll.

The only exception to the spinning procedure outlined above was the use of higher quench rates to prepare the low undrawn yarn birefringence samples BAL-9 and BAL-10. Modifications to the drawing procedure were made to prepare samples 15 thru 22. In drawing samples 15 and 16, the stretch heater temperature was set at 180°C instead of the customary 195°C to examine the effect of this variable. Samples 17 through 22 were annealed on the drawtwister at 195°C by passing the yarn 3 times over a triangular shrinkage heater adjacent to the drawing roll.

c. Woven Fabric Preparation

The 1050-175-1/2Z yarns for woven fabric were dountwisted to

TABLE III

PROPERTIES OF NYLON 6 DRAWN YARNS PREPARED FOR WOVEN BALLISTIC CLOTH

Identification	Description		Denier	UE %	UTS (gpd)	Toughness	Bkg. St. (lbs)	Uster	Birefringence
	Term.	-U. E.							
BAL-2	T-35-18		1054	18.2	8.90	.941	20.67	7.50	.05534
BAL-4	T-30-18		1047	18.3	8.83	.969	20.38	8.75	.05569
BAL-6	T-30-25		1062	25.6	7.68	1.309	18.18	10.00	.05310
BAL-8	T-30-14		1056	15.3	9.41	.779	21.90	5.00	.05612
BAL-10	T-30.18 Low biref.		1050	18.2	9.12	1.010	21.11	8.25	.05545
BAL-12	U-30-18		1049	18.5	8.70	.943	20.12	7.80	.05425
BAL-14	T-25-18		1057	18.6	8.84	.986	20.60	8.00	.05484
BAL-16	T-30-18 Low heater temp.		1050	17.4	8.92	.925	20.65	5.80	.05595
BAL-18	T-30-18 annealed		1047	18.8	9.05	1.003	20.89	6.00	.05977
BAL-20	T-25-18 annealed		1041	20.1	8.94	1.062	20.50	4.00	.05822
BAL-22	T-35-18 annealed		1052	19.9	8.83	1.019	20.48	6.80	.05671

TABLE IV

PROPERTIES OF NYLON 6 DRAWN YARNS PREPARED FOR BALLISTIC FELTS

Identification	Description		Denier	UE %	UTS (gpd)	Toughness	Bkg. St. (lbs)	Uster Birefringence
	Term.	-U. E.						
BAL-1	T-35-18		1047	18.1	9.09	.958	20.83	7.50 .05534
BAL-3	T-30-18		1049	19.1	8.50	.998	19.62	8.75 .05569
BAL-5	T-30-25		1070	24.9	7.54	1.305	17.25	10.00 .05310
BAL-7	T-30-14		1056	16.1	9.48	.834	22.03	5.00 .05612
BAL-9	T-30-18 Low biref.		1041	18.0	9.03	.970	20.75	8.25 .05545
BAL-11	U-30-18		1053	17.6	8.63	.899	20.02	7.80 .05425
BAL-13	T-25-18		1048	18.7	8.99	1.042	20.92	8.00 .05484
BAL-15	T-30-18 Low heater temp.		1050	18.5	8.95	.944	20.73	5.80 .05595
BAL-17	T-30-18 annealed		1069	20.3	8.96	1.077	21.08	6.00 .05977
BAL-19	T-25-18 annealed		1040	19.6	8.90	1.045	20.39	4.00 .05822
BAL-21	T-35-18 annealed		1065	19.5	8.69	1.003	20.42	6.80 .05671

insert 3-4 turns per inch Z twist and woven to a 2 x 2 basket weave construction with two ends weaving as one and two picks weaving as one. Reed width was 55-3/4 inches. The fabrics were finished in accordance with the guidelines of MIL-C-12369E (GL), 25 July 1968. They were scoured on a jig with 2% soda ash at 96°C for 60 minutes. This was followed with a 30 minute hot water (82°C) rinse and a 30 minute neutral pH cold water rinse. Finally, the fabrics were framed and heat set on a Kranz tenter frame. Exposure in the high heat zone was 30 seconds at 190°C. Previous work had indicated temperatures of this order would be required to meet the shrinkage standards of MIL-C-12369E(GL). The physical properties of the fabrics are given in Table V. The crystalline content of yarns removed from the fabrics is compared to that of its drawn yarn precursor in Table VI. The error in the X-ray analysis of any of the crystalline forms is believed to be $\pm 5\%$ of the value.

In a separate experiment, the effect of finishing conditions was investigated.

A sample of Allied Chemical Corporation Merge 5915, 1050-70-1/2Z, Type 1T70 nylon 6 yarn was woven into three samples of ballistic cloth as described above. One sample (BAL-23) of this cloth was retained for ballistic testing in the greige form. Another sample (BAL-24) was given a 60 minute scour at 98°C with 2% soda ash. This was followed by a 30 minute rinse with 82°C water and a 30 minute cold water rinse at neutral pH. The fabric was then framed and heat-set on a Krantz tenter frame at 190°C as were samples BAL-2 thru 22. The third sample (BAL-25) was scoured at 65°C with 2% soda ash for 60 minutes, and rinsed with 65°C water for 30 minutes. After a 30 minute cold water rinse, the fabric was dried on the tenter frame at 130°C.

d. Felt Preparation

The drawn fibers of odd numbered samples BAL-1 thru 21 were converted to ballwarps of approximately 100,000 denier. Three ballwarp ends were simultaneously fed into an unheated stuffer box crimper. The crimper was unheated to minimize disorientation of the yarn. The crimped tow was cut to 3.5 to 4.0 inch staple on conventional staple cutting equipment.

Several unsuccessful attempts were made to convert the staple to a carded web at National Felt Company, Easthampton, Massachusetts. The fiber had a tendency to become embedded in the card clothing and would not transfer from cylinder to cylinder. Efforts to improve runnability via speed changes reduced input rate, and varying card settings

TABLE V

PHYSICAL PROPERTIES OF WOVEN BALLISTIC FABRIC PER MIL-C-12369E-(CL)

Identification	Width (in.)	Weight (oz/yd ²)	Yarns per Inch		B.S. (lbs.)		U.E. (%)		Shrinkage (%)	
			W	F	W	F	W	F	W	F
BAL-2	48.9	14.4	47	44	1172	1116	54.4	49.3	2.7	1.3
BAL-4	48.8	14.0	47	44	1125	1117	55.9	51.8	2.4	1.4
BAL-6	49.1	14.6	47	43	1093	1028	63.8	58.1	2.5	1.7
BAL-8	48.3	15.2	48	45	1149	1061	60.1	48.1	1.4	1.0
BAL-10	48.6	14.6	47	43	1153	1111	58.8	54.2	2.8	1.9
BAL-12	48.5	14.3	48	43	1087	1023	54.9	52.9	2.6	1.7
BAL-14	48.6	14.9	47	44	1124	1068	62.7	53.8	2.0	1.0
BAL-16	47.9	15.1	48	45	1056	1048	61.2	55.9	1.9	1.1
BAL-18	48.3	14.5	47	44	1055	1035	58.8	55.8	2.2	1.3
BAL-20	48.9	14.2	46	43	887	909	46.9	48.9	2.2	1.5
BAL-22	48.3	14.8	47	44	1073	996	60.8	52.0	2.0	1.1

TABLE VI
PERCENT CRYSTALLINITY OF SAMPLES⁹

<u>Identification</u>	<u>Drawn Yarn</u>			<u>Yarn from Finished Fabric</u>		
	<u>Alpha</u>	<u>Beta</u>	<u>Gamma</u>	<u>Alpha</u>	<u>Beta</u>	<u>Gamma</u>
BAL-2	22	6	22	29	6	18
BAL-4	20	6	24	30	5	19
BAL-6	14	7	26	34	6	11
BAL-8	19	6	21	43	5	7
BAL-10	22	5	23	32	6	17
BAL-12	33	5	8	35	5	16
BAL-14	24	6	17	37	5	10
BAL-16	27	6	17	36	6	14
BAL-18	17	6	28	33	5	15
BAL-20	29	5	10	32	6	16
BAL-22	10	5	29	37	6	9

⁹. See Reference

were unsatisfactory. Addition of 0.2 - 0.4% cohesive antistat over-finish (Lenox Spinrite # 3256) prior to carding tended to further aggravate the problem. The staple was finally converted into a web on a small card by Felters Corporation, Middlebury, Massachusetts. There was considerable variation in weight and thickness between and within samples. The aerial density of the individual felt samples used in the ballistic test varied from 8.3 to 14.6 oz./sq. yd. This variation was the result of problems encountered in carding the staple. These difficulties may be attributed to low crimp amplitude and low crimp stability.

e. Ballistic Testing

1. Woven Fabric

Ballistic testing of the woven fabric was conducted at H. P. White Laboratory, Bel Air, Maryland in accordance with MIL-STD-662 and MIL-C-12369 E(GL). The projectile was a T-37, 17-grain, .22 caliber fragment simulator. Four V_{50} determinations were made on each sample. The ballistic test specimen consisted of 12 layers of unsupported 15 inch by 15 inch fabric between supports. The V_{50} may be defined as the velocity at which half the projectiles are stopped and half penetrate the test specimen. All of the test specimens were preconditioned in the test laboratory for 48 hours prior to testing. Data are shown in Table VII.

2. Felts

The felts were tested in accordance with MIL-STD-662 and IP/DES-S-53-7. The test specimen consisted of 5-6 layers of 18 inch by 18 inch unsupported felt between supports. The projectile was a T-37, 17-grain, .22 caliber fragment simulator. Relative rankings of V_{50} are shown in Table VIII. No sample displayed an advantage over commercially available materials. Actual data are available at United States Army Laboratories.

Phase II

a. Polymer Preparation

The polymer utilized in the Phase II study of the effect of filament denier was a sample of 25,000 Mn dibasic acid terminated polymer from Allied Chemical plant production. It closely approximates the polymer of samples BAL-14 and BAL-20 of Phase I.

TABLE VII

BALLISTIC PROPERTIES OF WOVEN FABRICS

<u>Identification</u>	<u>Description</u>	<u>V50</u>	<u>High Partial</u>	<u>Low Complete</u>	<u>Range of Mixed Results</u>
BAL-2	T-35-18	1270	1300	1237	64
BAL-4	T-30-18	1257	1272	1224	49
BAL-6	T-30-25	1230	1263	1193	71
BAL-8	T-30-14	1269	1296	1251	45
BAL-10	T-30-18 Low biref.	1244	1273	1198	75
BAL-12	U-30-18	1270	1289	1227	62
BAL-14	T-30-18	1246	1276	1220	59
BAL-16	T-25-18 Low heater temp.	1253	1281	1217	64
BAL-18	T-30-18 ann.	1256	1288	1233	54
BAL-20	T-25-18 ann.	1248	1276	1213	63
BAL-22	T-35-18 ann.	1248	1262	1233	29

TABLE VIII

BALLISTIC PROPERTIES OF NEEDLE-PUNCHED FELTS

<u>BAL</u>	<u>Type</u>	<u>Relative V₅₀</u>
1	T-35-18	66.2
3	T-30-18	71.7
5	T-30-25	95.4
7	T-30-14	79.5
9	T-30-low biref.	74.4
11	U-30-18	75.1
13	T-25-18	100.0
15	T-30-18-low heater	73.2
17	T-30-18-Ann.	81.0
19	T-25-Ann.	83.0
21	T-35-18-Ann.	76.3

b. Yarn Preparation

840 denier yarns with nominal filament deniers of 4, 6, 8, and 15 were spun and drawn to equivalent physical properties. Spinning and drawing were done on the same equipment described in Phase I. The experimental procedure was the same as that outlined except the spinning rate was reduced to 25.8 lbs./hr., and the drawing speed was reduced to 840 ft./min. These changes were made to ensure that equivalent strengths could be obtained from all samples. Data are shown in Tables IX and X.

c. Woven Fabric Preparation

Yarns BAL-26, -27, -29, and -30 were woven into 8 oz./sq. yd. plain weave Type II ballistic cloth according to amendment 2 to MIL-C-12369E (GL). Warp and filling yarns contained only a nominal half turn of producers twist. The fabrics were scoured on a jig with 2% soda ash at 96°C for 60 minutes. This was followed with a 30 minute hot water (82°C) rinse and a 30 minute neutral pH cold water rinse. Finally, the fabrics were framed and heat-set on a Krantz tenter frame. Exposure in the high heat zone was 30 seconds at 190°C. Fabric data are shown in Table XI.

d. Felt Preparation

A tow of 200-300 thousand denier was prepared from each of the experimental yarns. The tow was then crimped in a steam heated stuffer box texturizer. Essentially, equivalent conditions were employed with all yarns. As seen in the data in Table XII, the larger filament deniers had slightly less crimp as expected from their larger filament cross section. The crimped tows were then cut into 3.5 - 4.0-inch staple on conventional staple cutting equipment. The staple was shipped to the U. S. Army Natick Laboratories to be converted into felts and tested for ballistic resistance.

e. Ballistic Testing

Three V₅₀ determinations were made on each of the woven fabrics at H. P. White Laboratories in accordance with MIL-STD-662 and amendment 2 to MIL-C-12369E (GL). The projectile used was a T-37, 17-grain, .22 caliber fragment simulator. The rifling in the barrel was one revolution in 20 inches. The test panel consisted of sixteen plies of unsupported 15 x 15 in. fabric between supports. Data are shown in Table XIII.

TABLE IX

PROPERTIES OF NYLON 6 UNDRAWN YARNS
PREPARED FOR BALLISTIC STUDIES

Identification	Nominal Drawn Filament Denier	Denier/ Filament	FAV	Carboxyl (eq/10 ⁶ g)	Amine (eq/10 ⁶ g)	Uster	Biref.
BAL 26	4	3586/204	69	59	16	8.0	.0126
BAL 27	6	3712/136	70	56	16	6.0	.0099
BAL 28	8	3866/105	68	62	16	6.0	.0041
BAL 29	15	4071/56	71	58	16	5.5	.0049

TABLE X
PROPERTIES OF NYLON 6 DRAWN YARNS
PREPARED FOR BALLISTIC STUDIES

<u>Identification</u>	<u>Nominal Filament Denier</u>	<u>Denier/ Filament</u>	<u>UTS (gpd)</u>	<u>UE (%)</u>	<u>Toughness</u>	<u>B.S. (lbs.)</u>	<u>Biref.</u>
BAL 26	4	837/204	9.16	16.9	1.02	16.9	.056
BAL 27	6	837/136	9.02	16.7	1.09	16.7	.056
BAL 28	8	835/105	9.06	16.8	1.08	16.8	.058
BAL 29	15	846/ 56	9.06	16.9	1.09	16.9	.057

TABLE XI

PHYSICAL PROPERTIES OF WOVEN BALLISTIC FABRIC PER MIL-C-12369E (GL)

	Width (in.)	Weight (oz./yd ²)	Yarns/Inch		B.S. (lbs.)		U.E. (%)		Shrinkage (%)	
			W	F	W	F	W	F	W	F
BAL 26H	45.9	8.56	35.3	31.5	738	665	38.4	45.4	3.1	1.3
BAL 27H	45.9	8.54	35.0	32.3	744	624	41.7	39.8	3.2	1.7
BAL 28H	46.9	8.55	34.0	32.8	733	682	42.5	40.0	2.4	1.8
BAL 29H	46.7	8.50	34.3	32.0	638	681	38.6	41.2	2.4	0.9

TABLE XII

PROPERTIES OF STAPLE PREPARED FOR PHASE II

	Denier		Tenacity, g/d		Elongation, %		Crimp/In.
	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	
BAL 26S	4.19	0.37	7.86	0.72	38.7	3.57	11
BAL 27S	6.81	0.45	8.32	0.56	39.8	5.59	11
BAL 28S	9.73	1.11	7.06	1.26	35.8	6.29	9
BAL 29S	17.19	0.97	7.37	0.74	40.1	6.72	7

TABLE XIII

BALLISTIC PROPERTIES OF WOVEN FABRICS

<u>Identification</u>	<u>Nominal Filament Denier</u>	<u>V 50</u>	<u>High Partial</u>	<u>Low Complete</u>	<u>Range of Mixed Results</u>	<u>V 50</u>
BAL 26H	4	1242	1241	1229	12	1246
		1243	1284	1208	76	
		1253	1277	1219	58	
BAL 27H	6	1263	1291	1205	86	1252
		1238	1257	1182	75	
		1254	1281	1244	37	
BAL 28H	8	1247	1232	1260	-	1243
		1269	1222	1184	138	
		1228	1277	1207	70	
BAL 29H	15	1295	1325	1286	39	1262
		1252	1270	1225	45	
		1244	1241	1213	28	

5. Discussion

a. Woven Fabric

Tables II and III show the physical and chemical properties of nylon prepared for ballistic studies in woven cloth form. All of the samples conform to the experimental plan. The beneficial effect of annealing and low undrawn orientation are very apparent. Despite the fact that yarns differ significantly in toughness, tensile strength, elongation and orientation, there is only 5% difference in V_{50} . It would appear that several explanations are possible. The ballistic properties may be an intrinsic property of this material, i.e. in this woven structure differences in orientation and crystallinity play little effect, or some overriding factor such as fabric finishing conditions, yarn finish, or yarn twist tends to reduce the effect of these parameters. In fact, a sampling of the physical properties of yarns withdrawn from finished ballistic cloth, as well as the X-ray structure, indicates substantial changes have taken place in transforming the drawn yarn to a finished fabric. Toughness, which may be a measure of the energy absorbing power of a ballistic yarn, ranged only 12%. At the high rates of strain experienced in a ballistic cloth during testing, these differences may be considerably smaller.

To test the relative effect of different finishing conditions the ballistic properties of greige (unfinished), normally finished, and low temperature finished fabrics were compared. The results showed that the greige and normally finished fabric have V_{50} 100 ft./sec. higher. The alkaline scour normally given ballistic cloth removes the lubricating finishing. These results may indicate a critical relationship between yarn lubricity and changes in yarn structure caused by aqueous treatment and heat setting.

Since the results of Phase I indicated little was to be gained in varying yarn properties in the traditional construction, it was decided to investigate one yarn parameter which had not been given previous attention, namely filament denier. It was further decided to test the effect of filament denier in a construction in which the filaments were freer to exert their individual influence. The traditional structure of MIL-C-12369E (GL) requires 3-4 turns per inch of twist. Recent studies at U.S. Army Natick Laboratories had shown that excellent ballistic properties could be obtained from the lighter weight nylon ballistic cloth based on 840 denier yarns which contain only a nominal 0.5 turn/inch of producer twist. These findings have lead to a specification

for a Type II Ballistic Cloth (See Table XIV). Samples of Type II fabric were prepared from yarns with filament deniers of 4, 6, 8, and 15 of equivalent tensile strength and elongation. Both greige (off the loom) and finished fabric were supplied to the Natick Laboratories for studies of V₅₀ ballistic performance. The greige fabric was supplied to permit a study of the effect of finishing conditions to be conducted. At the time of the writing of this report, these results were not available. As seen in Table XIII, spot check of V₅₀ performance conducted by the contractor indicated no effect of filament denier on ballistic performance.

b. Felts

A review of studies of the factors which influence the ballistic properties of needle-punched felts¹⁰ suggested that although some crimp is necessary to manufacture felts, gains in V₅₀ could be achieved by eliminating crimp entirely. It was rationalized that uncrimped fiber had greater strength and presented greater opportunity for fiber-fiber contact. For the reasons presented above it appeared that lightly crimped staple which had experienced a minimum amount of disorientation would provide the best media to evaluate the nylon 6 parameters. This low disorientation was achieved by eliminating the steam on the stuffer box crimper. Unfortunately, the type of crimp imparted appeared to present some problems in preparing card webs for needle punching.

The V₅₀ of all the felts are shown on a relative scale in Table VIII. For this scale the V₅₀ of BAL-13 whose 25,000 \overline{M}_n and 18% elongation closely approximates the properties of commercially available material was given a value of 100. Inspection of this table shows that no sample had V₅₀ superior to BAL-13. These results indicate that little improvement in the ballistic properties of felt can be anticipated from additional modification of fiber molecular weight, elongation or crystallinity.

In Phase II of the study yarns with varying filament denier were textured with steam in the stuffer box to fully develop crimp. As seen in Table XII the larger filament deniers had slightly less crimp as expected from their larger filament diameter. The staple produced has been sent to United States Army Natick Laboratories for this evaluation.

TABLE XIV
PHYSICAL REQUIREMENTS OF CLOTH, BALLISTIC,
NYLON, AMENDMENT-2 MIL-C-12369E (GL)

	<u>Type I</u>	<u>Type II</u>
Yarn Denier	1050	840
Yarn Twist, turns/in.	3.4	0.5 producer
Weight, oz./yd. ² , min.	13.5	7.7
max.	15.0	8.3
Weave	Basket	Plain
Yarns/inch. (min.) Warp	46	33
Filling	42	32
Breaking Strength (min.) Warp	900	650
Filling	825	600
Ultimate Elongation (min.) Warp	25	35
Filling	20	35

6. Conclusions

Only marginal improvements in the ballistic properties of conventional ballistic cloth and felts can be made by altering nylon 6 fiber properties.

Finish conditions can be important to the development of maximum V₅₀ for any nylon 6 ballistic cloth.

Filament denier has little effect on V₅₀ in Type II ballistic cloth as tested.

7. Recommendations

The U.S. Army Natick Laboratories should continue to evaluate new textile structures for personnel armor. When improved new structures are found, this type of study should be conducted again.

The samples produced should be evaluated with other fragment simulators and with different sample thickness.

A study of the effect of nylon 6 finishing conditions on V50 should be conducted.

The effect of filament denier on ballistic properties should be evaluated in several needlepunched felt structures.

Felts from mixtures of low crimp staple from Phase I and high crimp staple from Phase II should be tested.

8. References

1. Sbrolli, W., "Nylon 6" in Man-Made Fibers: Science and Technology, Vol. 11, H. F. Mark, S. M. Atlas, E. Cernia, Eds., Interscience, New York, 1967.
2. Moncrief, R. W., Man-Made Fibers, Fifth Edition, p. 354, Interscience, New York, 1970.
3. Billmeyer, F. W., Textbook of Polymer Science, Second Edition, 519, Wiley-Interscience, New York, 1971.
4. Ziabicki, A., "Principles of Melt Spinning" in Man-Made Fibers: Science and Technology, Vol. 1, H. F. Mark, S. M. Atlas, E. Cernia, Eds., Interscience, New York, 1967.
5. McIntyre, J. E., "Man Made Fibers, Manufacture" in Encyclopedia of Polymer Science and Technology, Vol. 8, H. F. Mark, N. G. Gaylord, N. M. Bikales, Eds., Interscience Div., John Wiley and Sons, New York, 1968.
6. Hayes, B. T., P. V. Papero and D. C. Prevorsek, Allied Chemical Corporation, Fibers Division, Research Monograph M-12, May 1967.
7. Schaefgen, J. R. and P. J. Flory, J. Am. Chem. Soc. 70, 2709 (1948).
8. Twilley, I. C., U. S. Patent 3,386,967 (1968), to Allied Chemical Corporation.
9. Roldan, L. G., F. Rahl, and A. R. Paterson, J. Polymer Sci. C, No. 8, 145-158 (1965).
10. Laible, R. C. and M. C. Henry, A Review of the Development of Needlepunched Felts, U. S. Army, Natick Laboratories. Report Number 70-32-CE (T S - 167) p. 26, Oct. 1969.